Catalytic aerobic oxidation of lignin-derived bio-oils using oxovanadium and copper complex catalysts and ionic liquids

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ABSTRACT

Herein, we report the aerobic oxidation of several bio-oils (pyrolysis and microwave) derived from Kraft lignin using oxovanadium complex catalyst, $(HQ)_2V^V(O)(O^iPr)$ (HQ = 8-oxyquinoline) (**2**), ionic liquid (IL)-tagged oxovanadium complex, PF_6-IL-salen-$V^{IV}(O)$ (**3**) (PF_6 = hexafluorophosphate) and copper catalyst CuX/TEMPO/2,6-lutidine (**4**) [X = OTf, trifluoro-methanesulfonate), Cl; TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl]. Cleavage of some lignin linkages and reduced phenolic content were observed by multinuclear NMR spectroscopy, FT-IR and 1D/2D GC/MS analysis. Catalyst **2** oxidized chloroform extracts of the microwave bio-oil more extensively than those from the pyrolysis bio-oil although reactivity trends were similar. With catalyst **3** in [MMIM][MeOSO₃], the phenolic conversion was modest compared with the increase in carboxyl and decrease in aliphatic OH groups. IR spectra were consistent with phenol oxidation to quinone-type structures. In contrast, copper catalyst **4** showed formation of high molecular weight compounds after oxidation, likely resulting from radical recombination. Comparison of reactivity between the different types of lignin-derived bio-oils is also discussed.

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1. Introduction

Rapid depletion of petroleum and increasing environmental concerns are driving the exploration of new alternatives for petrochemicals. Lignocellulosic biomass is a promising candidate for the production of chemicals and materials [1]. It is constituted primarily of hemicellulose, cellulose and lignin; the latter is the most abundant non-food and renewable aromatic-containing macromolecule on Earth [2]. Despite the large production of lignin in the pulp and paper industry, this material has a limited usage, mostly as a low-grade fuel.

Pyrolysis can be used to liquefy lignin, facilitating transportation and storage and potentially increasing its economic value. In this process, lignin is heated rapidly between 500 and 700 °C in the absence of oxygen to produce a liquid bio-oil [3]. Pyrolysis of lignin also decreases the molecular weight through cleavage of β-O-4 linkages (Fig. 1) [4]. In a complementary technique, microwave reactors are used to produce bio-oils, avoiding temperature gradi-

ents and formation of the char by-product obtained from thermal heating [5].

Pyrolysis and microwave bio-oils have a high water and acid content [6] that triggers their decomposition through radical polymerization, generating an intractable mixture [7]. Due to this instability, valorization of lignin bio-oils has been limited to hydrodeoxygenation [8], catalytic pyrolysis [9], zeolite cracking [10] and steam-reforming [11], among others. Oxidation using inexpensive base metal catalysts and air is an attractive approach for the depolymerization of lignin [12]. However, oxidation of bio-oils to produce chemicals is scarce in the literature. Xu et al. oxidized bio-oils using ozone to convert the aldehyde content into acids that could then be esterified to improve the fuel properties [13]. Boateng et al. reported the production of smaller monomers from pyrolytic lignin using transition metal complexes such as copper, manganese, vanadium and iron [14]. Unfortunately, no further details of this work have yet appeared in the literature.

Baker et al. reported several oxovanadium (eg., **1** and **2**) and copper/TEMPO/pyridine [TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl] (**4**) catalysts for the selective cleavage of lignin models using air as terminal oxidant (Fig. 2) [15]. Control over C—C and C—H bond cleavage was achieved using different solvents and oxovanadium(V) catalysts [16]. In one example, cleavage of phenoxyethanol

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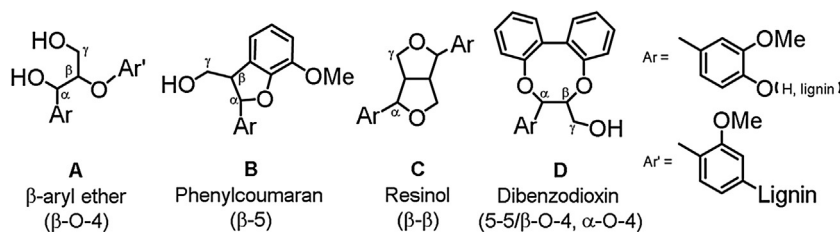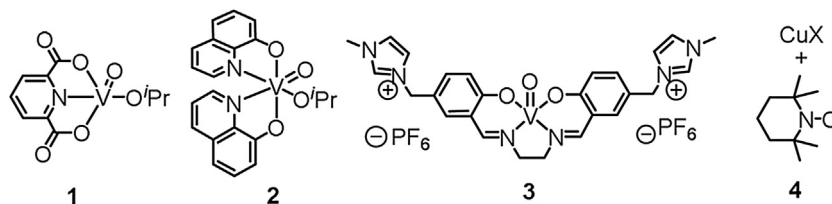
Fig. 1. Principal linkages in lignin.

Fig. 2. Oxovanadium and copper catalyst for the oxidation of bio-oils.

lignin models, containing the β-O-4 linkage (the most abundant in hardwoods), afforded mainly ketone and phenol by C—H bond cleavage, followed by C—C bond cleavage of the ketone intermediate (Scheme 1) [17]. In contrast, the Cu/TEMPO catalyst **4**, with the addition of 2,6-lutidine, effected the selective C—C bond cleavage of β-O-4 and β-1 lignin models, in spite of the poor carbon balance of these reactions [16a,b]. Recently, we showed that **1** and **2** are efficient catalysts for reducing the molecular weight of organosolv lignin, retaining the reactivity observed in lignin models [18].

As a solvent for bio-based transformations, ionic liquids (ILs) have the advantage of dissolving lignocellulosic biomass and allowing for fractionation into cellulose, hemicellulose and lignin components [19a]. Singer and co-workers reported that ionic liquid-tagged Co^{III}(salen) complex could be used as a catalyst with air/oxygen in ILs to selectively oxidize lignin model compound veratryl alcohol to veratryl aldehyde, allowing recycling of the catalyst and ionic liquid [19b]. Kervinen et al. reported an aerobic oxidation of veratryl alcohol to an aldehyde in aqueous media using Co(salen) complexes with various substituents [19c]. Zakzeski et al. reported that transition metal cobalt salts have shown better activity compared to Co(salen) and Co(porphryin) catalysts for the oxidation of lignin model compounds, Alcell lignin, and soda lignin in ionic liquids [19d]. A second advantage of ILs is their compatibility with microwave heating. It is known that microwave irradiation triggers heating by two main mechanisms – dipolar polarization and ionic conduction [19e]. Due to their ionic nature, ILs allow for highly effective interactions with microwave energy for accelerated reaction times and high product yields [19f].

Herein, we report the catalytic oxidation of pyrolysis and microwave bio-oils with oxovanadium -complex **2**, IL-tagged **3** and Cu/TEMPO/lutidine catalyst **4** (Fig. 2) using air as the terminal oxidant. The oxidized fractions were analyzed using IR and multinuclear NMR spectroscopy (^{1}H, ^{13}C UDEFT, and ^{31}P of derived phosphite esters) and GC/MS experiments.

2. Materials and methods

2.1. General considerations

^{1}H and ^{13}C{^{1}H} NMR spectra were obtained at room temperature on Bruker AV300 MHz, AV400 MHz or AV500 MHz spectrometers with chemical shifts (δ) referenced to the residual solvent signal. Deuterated solvents were purchased from Cambridge Isotope Laboratories and dried with molecular sieves. Acetonitrile (CH$_3$CN), chloroform (CHCl$_3$), dimethyl-sulfoxide (DMSO), diethyl ether (Et$_2$O), ethanol (EtOH), tetrahydrofuran (THF), dimethylformamide (DMF), ethyl acetate (EtOAc), chromium(III) tris(acetylacetonate), cyclo-hexanol, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP), N,N-diisopropylethylamine (DIPEA), CuCl, Cu(OTf)$_2$ (OTf = trifluoromethanesulfonate), TEMPO, 2,6-lutidine and VO(acac)$_2$ were purchased from Sigma Aldrich or Fisher Scientific and used without further purification. 1-Ethyl-3-methylimidazolium acetate, [EMIM][OAc], was purchased from Sigma Aldrich and dried under vacuum at 80 °C for 6–8 h prior to use. 1,3-Dimethylimidazolium methyl sulfate, [MMIM][MeOSO$_3$], was synthesized in our laboratories according to literature procedures [20]. Microwave and pyrolysis bio-oils were prepared by our collaborators at École Polytechnique and Western University, respectively, according to their reported procedures [5,21]. Oxygen was purchased from Linde Canada. Catalyst **2** was synthesized according to the published procedure [16d]. Quantitative ^{31}P NMR spectroscopy experiments were carried out following the reported procedure [22]. In order to prepare phosphitylation experiments, bio-oil samples were extracted with CHCl$_3$ or diethyl ether to reduce the water content. Solvents were then evaporated using a rotary evaporator followed by high vacuum. Under nitrogen atmosphere, 25 mg of bio-oil or the oxidized bio-oil residue was dissolved in 1.6:1 (v/v) of pyridine/CDCl$_3$ (500 μL) then 50 μL of TMDP and 5 μL of cyclohexanol were added to the solution. The reaction mixture was stirred for 10 min at room temperature and
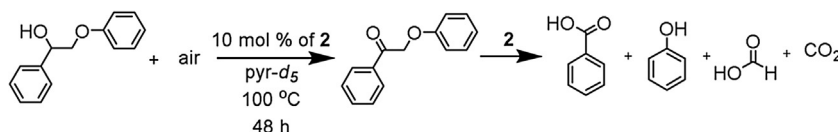
Scheme 1. Selective oxidation of phenoxyethanol lignin models using catalyst 2.

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